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EFFECT OF PHOSPHORUS OXIDE ADDITIVES ON THE COLOR AND PRODUCTION CONDITIONS OF $Bi_2O_3 – SiO_2 – P_2O_5$ GLASS

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Transparent glass has been obtained in the system $Bi_2O_3 – SiO_2 – P_2O_5$ with molar content 57.1% Bi_2O_3, 42.9 – 17.1% SiO_2, and 0 – 25.7% P_2O_5. It is found that the P_2O_5 content affects the glassmaking temperature and the glass color. Such glasses are promising for use in photonics and as scintillation materials.

Key words: glass production, bismuth-silicate glass, bismuth oxide, phosphorus oxide (V), color of glass.

Their unique combination of properties make bismuth-silicate glasses of interest as materials for making photoresists [1 – 3], optical storage devices, holographic systems, phase-conjugated optical devices [4], optical waveguides, fiber-optic amplifiers, oscillators [5], and others. Their initial oxide content ($2Bi_2O_3$; $3SiO_2$)[3] being the same as in silicoeulytine single crystals $Bi_4Si_3O_{12}$, they hold promise as scintillation materials [6] that can compete successfully with single crystals.

However, the long glassmaking time required to homogenize corrosive bismuth-containing melts at temperatures 1000 – 1200°C and their high viscosity make it difficult to obtain glass with good optical quality.

Partial replacement of the silicon oxide by phosphorus oxide, which is widely used as a glass forming agent, lower the melting temperature of the mix and the viscosity of melts, making the process of obtaining quality glass more practicable.

The objective of the present work is to obtain bismuth-silicate glass with the composition of silicoeulytine $2Bi_2O_3$; $3SiO_2$ with phosphorus oxide (V) replacing some of the silicon oxide in them.

The following ratios in moles of the initial components were used to make the glasses: $2Bi_2O_3$; $(3 – x)SiO_2$; $0.5xP_2O_5$, where x ranges from 0.1 (1.4% P_2O_5) to 2.5 (35.7% P_2O_5).

The mix was synthesized in a muffle furnace at temperature 740°C in 12 h with the sinter periodically removed from the furnace into an agate mortar. The synthesized material was melted in platinum crucibles in a resistance furnace at temperatures 900 – 1020°C. The soaking time of the melt varied from 1 to 3 h. The melts obtained were poured onto platinum foil cooled to temperature – 5°C.

Differential-thermal analysis (DTA) of the synthesized material was performed with a Derivatograph Q-1500D (MOM, Hungary) in platinum crucibles in the temperature interval 25 – 1000°C with heating rate 10 K/min.

Table 1 shows the ratios of the initial components of the mix used to make samples.

According to the DTA data,[4] replacement of part of the silicon oxide in the initial by phosphorus oxide (V) substantially lowers the melting temperature of the synthesized material (from 970°C for the composition $2Bi_2O_3$; $3SiO_2$ to 480°C for $2Bi_2O_3$; $1.2SiO_2$; $0.9P_2O_5$) (see Fig. 1).

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TABLE 1. Composition of the Initial Mix for Obtaining Glasses

Glass Sample No.	Mix compositions, mole fraction	Molar content, %		
		Bi_2O_3	P_2O_5	SiO_2
1	$2Bi_2O_3$; $3SiO_2$	57.1	–	42.9
2	$2Bi_2O_3$; $2.9SiO_2$; $0.05P_2O_5$	57.1	1.4	41.4
3	$2Bi_2O_3$; $2.7SiO_2$; $0.15P_2O_5$	57.1	4.3	38.6
4	$2Bi_2O_3$; $2.6SiO_2$; $0.2P_2O_5$	57.1	5.7	37.1
5	$2Bi_2O_3$; $2.52SiO_2$; $0.24P_2O_5$	57.1	6.9	35.9
6	$2Bi_2O_3$; $2.4SiO_2$; $0.3P_2O_5$	57.1	8.6	34.3
7	$2Bi_2O_3$; $2.3SiO_2$; $0.35P_2O_5$	57.1	10	32.9
8	$2Bi_2O_3$; $2SiO_2$; $0.5P_2O_5$	57.1	14.3	28.6
9	$2Bi_2O_3$; $1.5SiO_2$; $0.75P_2O_5$	57.1	21.4	21.4
10	$2Bi_2O_3$; $1.2SiO_2$; $0.9P_2O_5$	57.1	25.7	17.1

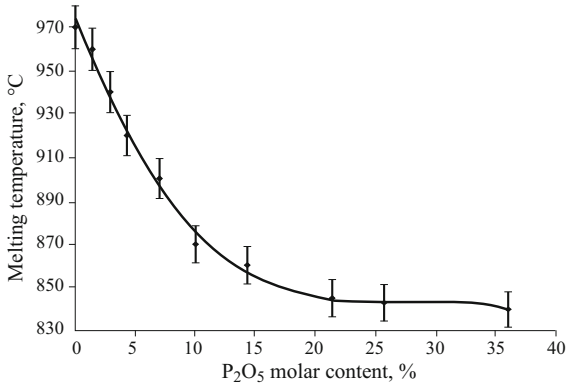

Fig. 1. Melting temperature of the synthesized materials versus their P_2O_5 content (according to DTA).

In addition, as the percentage content of the phosphorus oxide (V) increases, the melts become visually much less viscous.

Both factors make the process of obtaining quality glass, suitable for further study, more practicable.

Transparent glass samples, whose color depends on the mix composition and on the glassmaking time, were obtained for all compositions indicated (Table 2).

The color of the glasses in the system varied from light yellow to dark red. As the soaking time of the melt at the maximum glassmaking temperature with constant content of phosphorus oxide increases, the intensity of the glass color increases from yellow to dark red (see Table 2).

The phase composition of the samples was studied by the means of x-ray phase analysis (XPA) using a DRON-3 x-ray diffractometer. The XPA data confirm that the samples consist of a single phase and are amorphous.

TABLE 2. Color of Glass with Different Composition versus the Soaking Temperature and Time of Melt at the Maximum Glassmaking Temperature

Glass Sample No.	Melt soaking temperature, ± 10°C	Melt soaking time, h	Glass color
1	970	1.0	Yellow
		2.0	Red
2	960	1.0	Yellow
		1.5	Yellowish red
		2.0	Red
3	920	1.5	Yellow
		2.0	Yellowish red
4	915	2.0	Red
5	900	2.0	Red
		2.5	Dark red
6	880	2.0	Yellow
		2.5	Red
7	870	2.5	Reddish yellow
8	860	2.5	Reddish yellow
9	845	2.5	Light yellow
10	843	2.5	Light yellow

The optical quality of glasses depends on the presence of bubbles, cracks, sites of incomplete melting, and inclusions of foreign phases. Initially it was determined visually and then in transmission using a helium-neon laser.

The color differences of the glass could be due to a change of the ratio of the initial oxides as a result of their volatilization during glassmaking as well as the appearance of color centers as a result of a change of the valence state of the ions in the glass.

Differential-thermal studies showed that to within the sensitivity limits of the method the initial oxides do not volatilize on heating to 1000°C, since the mass of the initial mix remains unchanged irrespective of the phosphorus oxide (V) content.

According to the data of [7], the color change of the glasses is due to redox processes occurring with the participation of bismuth ions during glassmaking.

Increasing the phosphorus oxide (V) concentration in the initial mix gives a similar result, but color intensification slows down for molar content above 8.6%. This could be due to structural rearrangement of the glass as well as a change in the character of the redox processes.

CONCLUSIONS

Partial replacement of silicon oxide by phosphorus oxide in glasses with the composition $2Bi_2O_3$; $(3 - x)SiO_2$; $0.5xP_2O_5$ permits lowering considerably the melting temperature of the mix (by 20 – 130°C) and the viscosity of the melts, making the process of obtaining glasses of good optical quality more practicable.

As the phosphorus oxide (V) content in the initial mix increases, the color intensification of the glasses with increasing soaking time slows down, making it possible to obtain samples with color ranging from light yellow to dark red. These glasses hold promise for different applications in photonics and as scintillation crystals.

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